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(71) Applicant: S. C. JOHNSON COMMERCIAL MARKETS, INC. [US/US]; 8310 – 16th Street, Sturtevant, WI 53177–0902 (US).

(72) Inventors: TRUMBO, David, L.; 2509 North Main Street, Racine, WI 53402 (US). GLOOR, Paul, E.; 2820 Catherine Drive, Racine, WI 53402 (US).

(74) Agents: RYMARZ, Renee, J. et al.; S. C. Johnson Commercial Markets, Inc., Patent Section, 8310 – 16th Street, Sturtevant, WI 53177–0902 (US).

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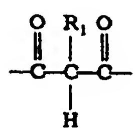


(I)

(57) Abstract

A novel single package aqueous polymeric formulation containing a polymeric ingredient having a latex seed core and both carboxylic acid functional pendant moieties and a monomer having pendant moieties having the ability to form stable enamine structures by reaction with amines which contain a divalent group of structure (I) wherein R_1 is either H, a C_1 to C_{10} alkyl group, or phenyl, is disclosed. Also disclosed is a process for preparing the aqueous polymeric formulation.

TITLE

CROSS-LINKABLE SURFACE COATINGS AND PROCESS OF PREPARATION

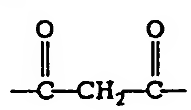
BACKGROUND OF THE INVENTION

Field of the Invention

This invention is related to a single-package aqueous polymeric formulation that contains a polymeric ingredient having a latex seed core and both acid functional and pendant moieties having the ability to form stable enamine structures by reaction with amines, e.g., acetoacetoxy functional pendant moieties. The invention is also directed to a process for preparing such aqueous polymeric formulations. The formulations of this invention are highly useful in protective coating compositions having ambient cure capability, e.g. wood, metal and concrete coatings.

Related Background Art

Ethylenically-unsaturated monomers containing active methylene groups such as



functional moiety-containing ingredients disclosed in U.S. Patent No. 5,498,659 may be used to provide desirable latex formulations, it has been found that the production of such formulations on a large scale is difficult.

Copending U.S. Applicantion No. 08/518,941, filed August 24, 1995, teaches ethylenically unsaturated 1,3-diketoamide functional compounds, polymers and latex formulations containing the same. Latexes made utilizing such unsaturated functional compounds possess improved hydrolytic stability.

The use of latex seeds in polymerization reactions to obtain latex polymers having uniform particle size is disclosed, for example, in U.S. Patent No. 5,189,107, U.S. Patent No. 4,122,136 and U.S. Patent No. 3,687,923. Copending U.S. Patent Application No. 08/539,808, filed October 5, 1995, describes the use of latex seeds in combination with the generation of a gradient polymeric morphology by varying the concentration ratio of the monomer feeds. None of these references disclose or suggest that novel single-package aqueous polymeric formulations could be prepared effectively on a large scale through the use of latex seed technology.

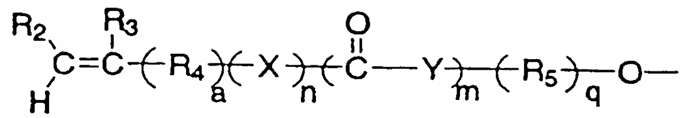
A high quality latex formulation including pendant moieties having the ability to form stable enamine structures by reaction with amines, e.g., acetoacetoxy functional pendent moieties, that can readily be prepared in an effective large scale manner will advantageously provide significant commercial advantage over prior art formulations.

The invention is also directed to an emulsion addition polymerization process for preparing the single package aqueous polymeric formulation. The process may be conducted as a single stage polymerization, but is preferably conducted as a multi-stage polymerization reaction so as to better control the properties of the resulting polymers. The process of this invention has been found to be particularly suitable for the preparation of large scale batches, e.g., 50 kg or greater, of an aqueous polymeric formulation that is subtantially free of grit, slime and gelation.

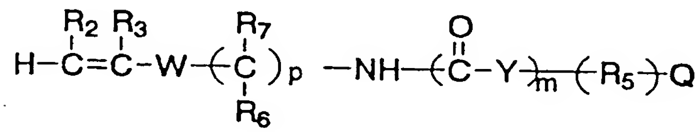
The polymeric formulation of this invention may be employed in adhesives and coatings, such as decorative or protective wood coating, paints, concrete coatings and the like.

DETAILED DESCRIPTION OF THE INVENTION

The polymeric ingredient employed in the aqueous polymeric formulation of this invention has incorporated therein latex seed particles having a number average particle size in the range from about 20 nanometers to about 60 nanometers. The preparation of such latex seed particles is well known to those skilled in the art. The latex seed particles used in this invention may be prepared using a single monomer or a mixture of monomers. A crosslinking agent may also be used if desired. A preferred latex seed particle of this invention is comprised of styrene and about 5 to 15% by weight of a divinylbenzene crosslinking agent. Preferably, this polystyrene latex seed has a number average particle size of 25 to 40 nanometers and most preferably of 33 to 35 nanometers. However, any latex seed particle within the above defined number average particle size range may be



or



wherein R_2 is either H, alkyl (i.e., C_1 to C_{10}), phenyl, substituted phenyl, phenylalkyl, halo, CO_2CH_3 or CN;

wherein R_3 is either H, alkyl (i.e., C_1 to C_{10}), phenyl, substituted phenyl, phenylalkyl or halo;

wherein R_4 is either alkylene (i.e., C_1 to C_{10}), phenylene, or substituted phenylene;

wherein R_5 is either alkylene or substituted alkylene;

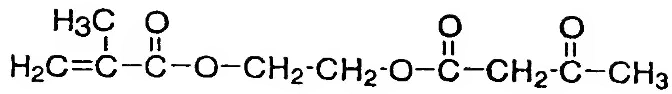
wherein R_6 and R_7 are independently either H, alkyl (i.e., C_1 to C_{10}), phenyl, substituted phenyl or phenylalkyl;

wherein any of "a", "m", "n", "p" and "q" is either 0 or 1;

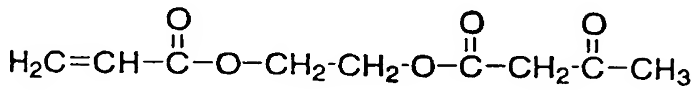
wherein each of "X" and "Y" is either —NH— or —O—;

wherein "W" is arylene having 6 to 20 carbon atoms;

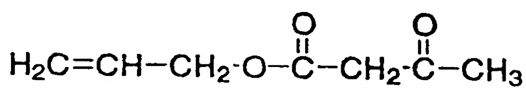
wherein "Q" is O or a single bond;



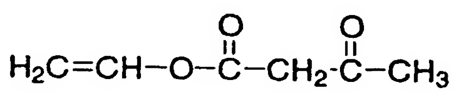
AAEA is structurally represented as:



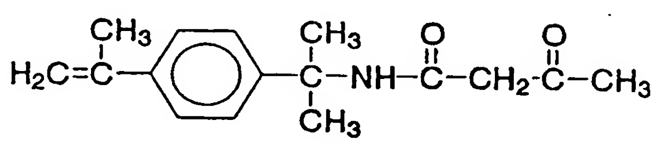
allyl acetoacetate is structurally represented as:



vinyl acetoacetate is structurally represented as:



and 3-isopropenyl-α,α-dimethylbenzyl amidoacetoacetate is structurally represented as:



Particularly preferred ethylenically-unsaturated acetoacetoxy-type functional moiety-containing ingredients are acetoacetoxyethyl methacrylate ("AAEM"), acetoacetoxyethyl acrylate ("AAEA"), and combinations thereof.

The carboxylic acid functional pendant moieties are derived from ethylenically-unsaturated carboxylic acid moiety-containing monomers. Those suitable for purposes of the invention include, but are not limited, to acrylic acid, methacrylic acid, fumaric acid-

Suitable water-soluble initiators include but are not limited to peracetic acid; certain perborates; certain percarbonates; certain perphosphates; certain persulfates, such as sodium, potassium, ammonium, and barium persulfate; acetyl peroxide; hydrogen peroxide; hydroperoxides such as tertiary-butyl hydroperoxide; and combinations thereof. A presently preferred water-soluble free-radical initiator is ammonium persulfate.

Suitable azo initiators include but are not limited to azodiisobutyl nitrile; azobisdimethyl valeronitrile; azodiisobutyl amide; azobis(alpha-ethylbutyl nitrile); azobis(alpha, gamma-dimethyl-capronitrile); and combinations thereof.

One redox combination, suitable for purposes of the present invention, may consist of a water-soluble persulfate as the oxidizing component of the redox combination, and a hydrosulfite, e.g. sodium hydrosulfite, as the reducing component of the redox combination. It is also possible to use water-soluble bisulfites, metabisulfites and/or thiosulfates, and formaldehyde sulfoxylates in lieu of the hydrosulfites.

Industrial Applicability

The single package aqueous polymeric formulations of this invention can be utilized to produce surface coatings as floor polishes, paints, adhesives and so forth. More particularly, these compositions produce durable, abrasion-resistant and solvent-resistant surface coatings or finishes on various substrates such as cardboard, concrete, counter tops, floors, marble and terrazzo, paper, stone, tile, wood and a variety of metal surfaces including polished metal surfaces and metal foils.

especially in relation to the production of rotogravure coatings.

Yet another specific end use for the polymeric formulations of the present invention is in the production of a wide assortment of architectural surface coatings which need to form films of various thicknesses, at relatively low temperatures, from about 25°C to about 0°C and yet which provide desirable surface hardness and durability qualities, due to their crosslinked polymeric structure.

The novel polymeric formulation of this invention can, moreover, be shipped in bulk-sized quantities or in various smaller-sized containers, as desired. For example, to satisfy certain industrial users, the formulation of this invention can readily be shipped in 55-gallon drums, or in larger quantities such as in rail cars, if desired. Yet, if consumers desire smaller, more conveniently-sized volumetric quantities, the polymeric formulation can be sold in 1-gallon or smaller containers or even in conventional aerosol containers.

The polymeric formulations of this invention are susceptible to embodiment in various forms. Described below are several presently preferred embodiments, with the understanding that these embodiments are merely examples of the present invention and are not limiting thereof.

The term "dispersion" as used herein means a two-phase system of which one phase consists of finely-divided particles, often in the colloidal-size range, distributed throughout a bulk substance, wherein such finely-divided particles provide the disperse or

the weight-average molecular weight ("Mw") value of such a polymeric ingredient is typically between about 2,000 and 50,000. Preferably, such a polymeric ingredient has an acid number in the range of about 50 to about 150 and a Mw value of about 2,000 to about 40,000, and more preferably a Mw value of about 2,000 to about 30,000.

However, in the case where there are at least two different polymeric ingredients, the polymeric ingredient having acetoacetoxy functional pendant moieties typically has an Mw value of about 2,000 to about 1,000,000. Preferably, the Mw value is between about 5,000 and about 500,000; more preferably, the Mw value is between about 15,000 and about 300,000; and most preferably, the Mw value is between about 50,000 and about 200,000. In this case the polymeric ingredient possessing acid functionality may only be polymeric in structure. Such a polymeric ingredient also preferably has an acid number in the range of about 50 to about 150 as well an Mw value of preferably about 2,000 to about 40,000, more preferably about 2,000 to about 30,000.

The polymeric formulation of this invention includes a polyfunctional amine containing compound. The polymeric formulation is delivered as a single-package composition. The single-package composition is prepared by mixing the polymeric ingredient and polyfunctional amine containing compound together and storing the mixture until use.

The preferred polyfunctional amine-containing compound, possessing at least two amine-functional moieties, is a non-polymeric polyfunctional amine-containing compound which typically has a chemical formula weight of less than about 2,000 grams per mole, and preferably has a

sulfate, potassium 2-ethyl hexyl sulfate, sodium nonyl sulfate, sodium lauryl sulfate ("NaLS"), potassium methylbenzene sulfonate, potassium toluene sulfonate, and sodium xylene sulfonate; higher fatty alcohols, for example, stearyl alcohols, lauryl alcohols, and so forth, which have been ethoxylated and sulfonated; dialkyl esters of alkali metal sulfosuccinic acid salts, such as sodium or potassium diamyl sulfosuccinates, in particular sodium dioctyl sulfosuccinate; various formaldehyde-naphthalene sulfonic acid condensation products; alkali metal salts, as well as partial alkali metal salts, and free acids of complex organic phosphate esters; and combinations thereof.

Examples of non-ionic surfactants which can be used to prepare the polymeric formulation of this invention include but are not limited to polyesters, for example, ethylene oxide and propylene oxide condensates which include straight and/or branched chain alkyl and alkaryl polyethylene glycol and polypropylene glycol ethers and thioethers; alkyl-phenoxy poly(ethyleneoxy) ethanols having alkyl groups containing from about 7 to about 18 carbon atoms and having from about 4 to about 240 ethyleneoxy units, such as heptyl-phenoxy poly(ethyleneoxy) ethanols, nonyl-phenoxy poly(ethyleneoxy)ethanols, and so forth; the polyoxyalkylene derivatives of hexitol, including sorbitans, sorbides, mannitans, and mannides; partial long chain fatty-acid esters, such as the polyoxyalkylene derivatives of sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan monooleate, and sorbitan trioleate; the condensates of ethylene oxide with a hydrophobic base, such as a base that is formed by condensing propylene oxide with propylene glycol; sulfur-containing condensates, for example, those

The emulsion-polymerizable mixture includes at least one acetoacetoxy functional moiety-containing monomeric ingredient and at least one acid moiety-containing monomeric ingredient, which is typically ethylenically-unsaturated.

The emulsion-polymerizable mixture may optionally further include other types of ethylenically unsaturated monomers, i.e., those containing at least one polymerizable carbon-to-carbon unsaturated double bond, provided that any such additional optional ingredient is addition-polymerizable with the acetoacetoxy functional moiety-containing and acid moiety-containing ingredients described above.

These compounds are well known and include, for example, C_2 to C_{20} alkenes, C_3 to C_{20} alkadienes, C_5 to C_{20} alkatrienes, C_5 to C_{20} cycloolefins, vinyl substituted aromatics, acrylic or methacrylic acid, C_1 to C_{20} alkyl esters of acrylic acid or methacrylic acid, C_6 to C_{20} aryl esters of acrylic or methacrylic acid, C_7 to C_{20} aralkyl esters of acrylic or methacrylic acid and the like.

More particularly, such ethylenically unsaturated monomers include, without limitation, ethylene, propylene, 1-butene, 2-butene, isobutene, 1-pentene, 2-methyl-2-butene, 1-hexene, 4-methyl-1-pentene, 3,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene, 6-ethyl-1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene, allene, butadiene, isoprene, chloroprene, 1,5-hexadiene, 1,3,5-hexatriene, divinylacetylene, cyclopentadiene, dicyclopentadiene, norbornene, norbornadiene, methylnorbornene, cyclohexene, styrene, alpha-chlorostyrene, alpha-methylstyrene, allylbenzene, phenylacetylene, 1-phenyl-1,3-butadiene, vinylnaphthalene, 4-methylstyrene, 4-methoxy-3-

benzoate, vinyl butyral, vinyl chloroacetate, isopropenyl acetate, vinyl formate, vinyl methoxyacetate, vinyl caproate, vinyl oleate, vinyl adipate, methyl vinyl ketone, methyl isopropenyl ketone, methyl alpha-chlorovinyl ketone, ethyl vinyl ketone, hydroxymethyl vinyl ketone, chloromethyl vinyl ketone, allilydene diacetate, methyl vinyl ether, isopropyl vinyl ether, butyl vinyl ethers, 2-ethylhexyl vinyl ether, 2-methoxyethyl vinyl ether, 2-chloroethyl vinyl ether, methoxyethoxy ethyl vinyl ether, hydroxyethyl vinyl ether, aminoethyl vinyl ether, alpha-methylvinyl methyl ether, divinyl ether, divinylether of ethylene glycol or diethylene glycol or triethanolamine cyclohexyl vinyl ether, benzyl vinyl ether, phenethyl vinyl ether, cresyl vinyl ether, hydroxyphenyl vinyl ether, chlorophenyl vinyl ether, naphthyl vinyl ether, dimethyl maleate, diethyl maleate, di(2-ethylhexyl) maleate, maleic anhydride, dimethyl fumarate, dipropyl fumarate, diamyl fumarate, vinyl ethyl sulfide, divinyl sulfide, vinyl p-tolyl sulfide, divinyl sulfone, vinyl ethyl sulfone, vinyl ethyl sulfoxide, vinyl sulfonic acid, sodium vinyl sulfonate, vinyl sulfonamide, vinyl benzamide, vinyl pyridine, N-vinyl pyrollidone, N-vinyl carbazole, N-(vinyl benzyl)-pyrrolidine, N-(vinyl benzyl) piperidine, 1-vinyl pyrene, 2 isopropenyl furan, 2-vinyl dibenzofuran, 2-methyl-5-vinyl pyridine, 3-isopropenyl pyridine, 2-vinyl piperidine, 2-vinyl quinoline, 2-vinyl benzoxazole, 4-methyl-5-vinyl thiazole, vinyl thiophene, 2-isopropenyl thiophene, indene, coumarone, 1-chloroethyl vinyl sulfide, vinyl 2-ethoxyethyl sulfide, vinyl phenyl sulfide, vinyl 2-naphthyl sulfide, allyl mercaptan, divinyl sulfoxide, vinyl phenyl sulfoxide, vinyl chlorophenyl sulfoxide, methyl vinyl sulfonate, vinyl sulfoanilide and the like.

During the reaction-hold period, while the emulsion-polymerizable ingredients are addition-polymerizing, it may be desirable to incorporate certain additional amounts of initiator or initiators, into the agitated reactor contents, to achieve a desired degree or percentage of conversion or reaction of polymerizable ingredients. Such additional amounts of initiator or ingredients may be the same as or may be different from the initiator ingredient or ingredients selected initially. Again, optional chain-transfer agent may be used, if desired.

For purposes of controlling the viscosity value of the polymeric formulation, it may be necessary to regulate the molecular weight of the polymer being formed. This can be accomplished by the incorporation into the reactor contents of a suitable chain-transfer agent. Suitable chain-transfer agents, to achieve this purpose, are well-known and include various halo-organic compounds such as carbon tetrabromide and dibromodichloromethane; sulfur-containing compounds such as the aklythiols including ethanethiol, butanethiol, tert-butyl and ethyl mercaptoacetate, as well as the aromatic thiols; and various other organic compounds having hydrogen atoms which are readily abstracted by free radicals during polymerization.

The amount of chain-transfer agent needed to achieve a particular molecular weight, moreover, can be estimated by the use of the Mayo equation. (See e.g., pages 226-233 of a text entitled Principles of Polymerization, second edition, by George Odian, published 1981 by John Wiley & Sons, Inc.)

Additional suitable chain-transfer agents or ingredients include but are not limited to butyl mercapto propionate; iso octyl mercapto propionic acid;

As noted previously, a suitable polyfunctional amine-containing compound having at least two amine-functional moieties is also incorporated into the aqueous polymeric emulsion before storage (a single-package composition). Whereas one skilled in the art would expect the polyfunctional amine ingredient of the formulation to crosslink with the acetoacetoxy functional groups via enamine formation in a single-package system, and thereby cause gellation, surprisingly, such gellation may be avoided. Without being bound to theory, it is believed that the mechanism for stabilization of the formulation containing both acetoacetoxy functional groups and carboxyl functionality is complex and probably results from (a) the base competing with the polyfunctional amine in reaction with the acetoacetoxy groups, thereby reducing the degree of crosslinking in the liquid state, and (b) the base neutralizing carboxylic acid groups on the polymer, thereby forming carboxylate ions, which would increase the solubility of the polymer and thereby lead to swelling rather than to agglomeration.

In such single-package formulations, it is believed that at least some of the crosslinking, or in certain situations a major portion of the crosslinking, may be taking place in the liquid phase, possibly within several (i.e., 1 to 4) hours of adding the polyfunctional amine. Accordingly, while not wanting to be tied to conjecture, yet desirous of providing a complete disclosure, it is presently postulated that addition of base to the reactor contents containing both acetoacetoxy functional groups and carboxyl functional groups may (1) compete with the amine-functional moieties vis-a-vis the acetoacetoxy functional moieties, thereby reducing the degree of crosslinking, and/or (2) enhance the colloidal

combinations of these, and so forth.) As noted previously, the most preferred amines are volatile, such as ammonia and other volatile amines.

The polymeric formulations of this invention may also be prepared using an emulsion polymerization reaction conducted, for example, by performing the step of introducing a major portion of the total amount of initiator, surfactant, optional chain-transfer agent, and evaporable aqueous carrier into the reaction vessel, in the manner described above, and separately performing the step of pre-emulsifying the emulsion-polymerizable mixture in a minor portion of the total amount of initiator, surfactant, optional chain-transfer agent, and evaporable aqueous carrier, for purposes of producing a pre-emulsion mixture; and, thereafter, performing the step of introducing the pre-emulsion mixture into the reaction vessel which already contains the major portion amounts of initiator, surfactant, optional chain-transfer agent, and evaporable aqueous carrier. Preferably, the reaction vessel is heated to the desired reaction temperature prior to adding the pre-emulsion.

In yet another preferred embodiment of the invention, the polymeric formulation of the present invention includes a mixture of at least two polymeric ingredients. A first polymeric ingredient includes pendant moieties having the ability to form stable enamine structures by reaction with amines, e.g., acetoacetoxy functional pendant moieties; and a second polymeric ingredient includes acid-functional pendant moieties. Indeed, it is not necessary to have both functionalities in a single polymeric ingredient to achieve satisfactory storage stability of the formulation as well as satisfactory crosslinkability of the resultant polymeric surface coating. In

al.; in U.S. Pat. No. 4,529,787 to Schmidt et al.; and in U.S. Pat. No. 4,546,160 to Brand et al.

As was mentioned above, it is believed that the above discussed polymeric ingredients containing the acetoacetoxy functional pendent moieties do crosslink to some degree with the amine-functional moieties of the polyfunctional amine when the latter is added to the formulation having carboxyl functionality. It is believed that the lack or delay in onset of gelation may be a result of the presence of the base ingredient in the reactor contents. Thus, the presence of the base in the single-package polymeric formulation of this invention is highly preferred.

The most preferred method of preparing the aqueous polymeric formulation of this invention employs a multi-stage polymerization process. As previously described, first the reactor is charged with (i) latex seed particles having a number average particle size in a range from about 20 manometers to about 60 nanometers, (ii) an initiator, (iii) a surfactant and (iv) an evaporable aqueous carrier. These ingredients are heated with agitation to a desired reaction temperature, typically 40°C to 90°C, more preferably 75°C to 85°C over a predetermined period of time, e.g. 30 minutes. More preferably, the initiator is combined with an amount of aqueous evaporable carrier and separately charged to the reactor after the introduction of the latex seed particles, surfactant and evaporable aqueous carrier.

Next, the emulsion polymerizable ingredients of the first stage are added to the emulsion polymerization reactor. The emulsion polymerizable ingredients of the first stage comprise at least one addition polymerizable ethylenically unsaturated monomer,

ethylenically unsaturated monomer. Preferably, the emulsion polymerization ingredients of the second stage contain a monomer containing pendant moieties having the ability to form stable enamine structures by reaction with amines, e.g., an acetoacetoxy functional monomer, or an acid functional monomer, most preferably an acetoacetoxy or 1,3-diketoamide functional monomer.

The emulsion polymerizable ingredients of the second stage may be introduced to the reactor by single or multiple monomer feeds, as desired. The second stage emulsion polymerizable ingredients are fed to the reactor containing the first stage polymeric ingredient having a latex seed core for a predetermined period of time, typically about 30 to about 90 minutes, while the desired second stage polymerization reaction temperature is maintained generally between about 40°C and 90°C, more preferably between 75°C to 85°C. Prior to incorporation of the second monomer mixture into the agitated reactor, however, additional water, surfactant, initiator, and/or optional chain-transfer agent may be added, as desired.

Preferably, the second-stage polymerizable ingredients contains a crosslinking ingredient or agent. In this regard, crosslinking agents that are suitable for purposes of the present invention include but are not limited to divinyl benzene, 1,6-hexanediol diacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylol propane triacrylate, trimethylol propane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, allyl acrylate, allyl maleate, allyl methacrylate, diallyl maleate, polyethylene glycol diacrylate, and polyethylene glycol dimethacrylate. If employed, the concentration of the crosslinking agent in the second stage polymerizable ingredients is generally in the

functional monomer, and at least one acid functional monomer.

During the later-stage reaction-hold periods, while the ingredients of the later-stage monomer mixture are addition-polymerizing in the presence of the dissolved or swollen latex particles of the preceding-stage polymerization, it may be desirable to incorporate further amounts of initiator into the agitated reactor contents to achieve desired conversion of later-stage reaction. Upon achieving the desired final-stage reaction conversions, then the pH of the reactor contents may be suitably adjusted, preferably using aqueous ammonia or other base, as previously described, to a pH above 7 and typically in the range of 8 to 9.75. At such pH conditions, the aqueous polymeric emulsion typically consists of insoluble latex particles of final-stage polymer, dispersed throughout the continuous phase of the emulsion.

As was briefly noted above, desired crosslinking, in accordance with one of the several, above-noted features of the present invention, occurs when the acetoacetoxy functional moieties desirably react with the amine-functional moieties of the polyfunctional amine. As noted above, the aqueous polymeric formulation of this invention includes carboxyl functionality in a single-package formulation that preferably includes an effective amount of base, "particularly volatile base", i.e., a base having a relatively high vapor pressure such as ammonia, for inhibiting undesirable reaction between the pendant moieties of the polymeric particles having the ability to form stable enamine structures by reaction with amines and the amine-functional moieties of the polyfunctional amine-containing compound, which would otherwise result in gelation. The desirable reaction,

of this invention possesses at least two amine-functional moieties, preferably, for best latex stability, has a chemical-formula weight of less than about 2,000 grams per mole, and preferably has a chemical-formula weight of less than about 1,000 grams per mole. The non-polymeric polyfunctional amines suitable for purposes of the present invention include aliphatic and cycloaliphatic amines having 2 to 10 primary and/or secondary amino groups and 2 to 100 carbon atoms.

Still further in this regard, suitable non-polymeric polyfunctional amines include but are not limited to hexamethylene diamine; 1,5 hexanediamine; 2-methyl pentamethylene diamine; 1,3-diamino pentane; dodecane diamine; 1,2-diamino cyclohexane; 1,3-diamino cyclohexane; para-phenylene diamine; 3-methyl piperidine; isophorone diamine; bis-hexamethylene triamine; diethylene triamine; and combinations thereof.

Other non-polymeric polyfunctional amines, which are suitable, include those containing adducts of ethylene and propylene oxide, such as the "JEFFAMINE" series D, ED and T of Texaco Chemical Company of Houston, Texas, U.S.A.

Preferred non-polymeric polyfunctional amines include 2 to 4 primary amino groups and 2 to 20 carbon atoms. Particularly preferred non-polymeric polyfunctional amines include hexamethylene diamine, diethylene triamine, and combinations thereof.

Until use is desired, the thus-produced crosslinkable, novel aqueous single package polymeric formulation can, for example, be stored at room temperature in a conventional container such as a metal can, a

were then flushed with water. The resulting polystyrene seed latex had a number average particle sized of 38 ± 5 nanometers and about 32% by weight solids.

Example 2

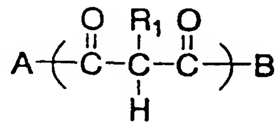
A single package aqueous polymeric formulation was prepared by a multi-stage emulsion polymerization. The polymerization reaction system consisted of a reactor or emulsion polymerization reaction zone equipped with agitation means and an inlet to receive polymerizable reactants.

The reactor was charged with the polystyrene seed latex (352 kg) prepared in accordance with the procedure described in Example 1, sodium lauryl sulfate (78 kg) and water (4,254 kg). The reaction mixture was heated to 80°C with agitation. The 80°C reaction temperature was maintained throughout the polymerization reaction. A 20% APS solution (78 kg) in water was charged to the reactor and the reactor contents held for 5 minutes. Next, a first monomer feed was prepared containing styrene (123 kg), methyl methacrylate (659 kg), methacrylic acid (69 kg), acetoacetoxyethyl methacrylate (131 kg) and 2-ethylhexyl acrylate (309 kg). The first monomer feed was introduced to the reactor at a feed rate of 21.5 kg/min. followed by a 15 minute hold time. The reactor contents were then neutralized by the addition of an aqueous ammonia (3%) solution (191 kg) at a feed rate of 38 kg/min. Next, a second monomer feed containing styrene (210 kg), butyl acrylate (803 kg), 1,6-hexane diol diacrylate (57 kg) and acetoacetoxyethyl methacrylate (38 kg) was added to the reactor contents at a feed rate of 36.9 kg/min. The reactor contents were then held for 15 minutes. A third monomer feed of styrene (850 kg) was then introduced to the reactor at a feed rate of 17 kg/min

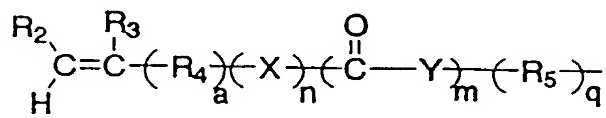
tested against catsup, mustard, coffee, tea, wine and vinegar.

Other variations and modifications of this invention will be obvious to those skilled in this art. This invention is not to be limited except to set forth in the following claims.

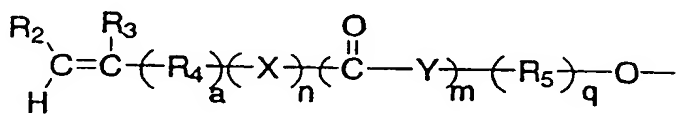
ability to form stable enamine structures are derived from a monomeric ingredient represented by the following structure



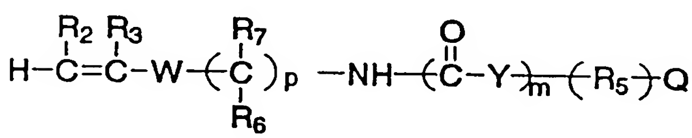
wherein R_1 is either H, a C_1 to C_{10} alkyl group, or phenyl; wherein A is either:



or



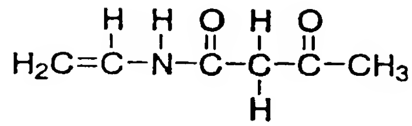
or

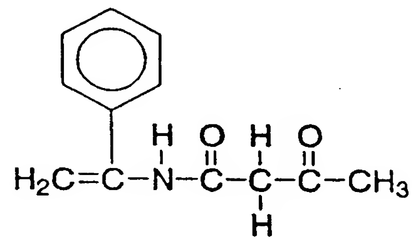


wherein R_2 is either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl, phenylalkyl, halo, CO_2CH_3 or CN;

wherein R_3 is either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl, phenylalkyl or halo;

wherein R_4 is either C_1 to C_{10} alkylene, phenylene, or substituted phenylene;





and combinations thereof.

8. An aqueous polymeric formulation according to claim 6, wherein the monomeric ingredient is selected from the group consisting of acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, allyl acetoacetate, vinyl acetoacetate, 3-isopropenyl-α,α-dimethylbenzyl amidoacetoacetate and combinations thereof.

9. An aqueous polymeric formulation according to claim 6, wherein the monomeric ingredient is selected from the group consisting of acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, and combinations thereof.

10. An aqueous polymeric formulation according to claim 1, wherein the acid functional moieties present in the polymeric ingredient are derived from a monomeric ingredient which is an ethylenically-unsaturated carboxylic acid moiety-containing monomer.

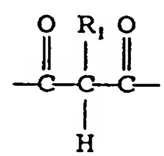
11. An aqueous polymeric formulation according to claim 10, wherein the monomeric ingredient is selected from the group consisting of acrylic acid, ethacrylic acid, fumaric acid-monoethyl ester, fumaric acid,

methacrylate, 2-ethylhexyl acrylate, butyl acrylate and mixtures thereof.

17. An aqueous polymeric formulation according to claim 16, wherein the number average particle size of said latex seed core is in a range from about 20 nanometers to about 40 nanometers.

18. A single-package aqueous polymeric formulation comprising:

(a) a first polymeric ingredient having acid functional pendant moieties and a second polymeric ingredient having pendant moieties having the ability to form stable enamine structures by reaction with amines which contain a divalent group of the structure



wherein R_1 is either H, a C_1 to C_{10} alkyl group, or phenyl, wherein both said first and second polymeric indredients have a latex seed core with a number average particle size in a range from 20 nanometers to about 60 nanometers;

(b) a polyfunctional amine having at least two amine functional moieties;

(c) an effective amount of base to inhibit crosslinking of the second polymeric ingredient with the polyfunctional amine; and

(d) an evaporable aqueous carrier.

wherein R_3 is either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl, phenylalkyl or halo;

wherein R_4 is either C_1 to C_{10} alkylene, phenylene, or substituted phenylene;

wherein R_5 is either alkylene or substituted alkylene;

wherein R_6 and R_7 are independently either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl or phenylalkyl;

wherein any of a, m, n, p and q is either 0 or 1;

wherein each of X and Y is either —NH— or —O-;

wherein W is arylene having 6 to 20 carbon atoms;

wherein Q is O or a single bond;

and wherein B is A, a C_1 to C_{10} alkyl group or phenyl, substituted phenyl, or heterocyclic.

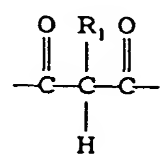
21. An aqueous polymeric formulation according to claim 20, wherein said first polymeric ingredient has an acid number in a range of from about 30 to about 300.

22. An aqueous polymeric formulation according to claim 21, wherein said polyfunctional amine is a non-polymeric functional amine having a chemical formula weight of less than about 2000 grams per mole.

23. An aqueous polymeric formulation according to claim 22, wherein said base is ammonia or a volatile amine.

nanometers to about 60 nanometers, (ii) an initiator, (iii) a surfactant and (iv) an evaporable aqueous carrier, to an emulsion polymerization reaction zone;

(b) introducing emulsion polymerizable ingredients to the emulsion polymerization reaction zone, said emulsion polymerizable ingredients comprising at least one monomer having pendant moieties having the ability to form stable enamine structures by reaction with amines which contain a divalent group of the structure



wherein R_1 is either H, a C_1 to C_{10} alkyl group, or phenyl, and at least one acid functional monomer, and polymerizing said emulsion polymerizable ingredients to form a polymeric ingredient;

(c) adding an effective amount of base to the aqueous carrier containing said polymeric ingredient to inhibit crosslinking of the polymeric ingredient with a polyfunctional amine while both are present in the aqueous carrier; and

(d) adding a polyfunctional amine having at least two amine functional moieties to the evaporable aqueous carrier containing said polymeric ingredient.

29. An addition polymerization process according to claim 28, wherein said latex seed particles are derived from styrene.

wherein R_5 is either alkylene or substituted alkylene;

wherein R_6 and R_7 are independently either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl or phenylalkyl;

wherein any of a, m, n, p and q is either 0 or 1;

wherein each of X and Y is either —NH— or —O-;

wherein W is arylene having 6 to 20 carbon atoms;

wherein Q is O or a single bond;

and wherein B is A, a C_1 to C_{10} alkyl group or phenyl, substituted phenyl, or heterocyclic.

31. An addition polymerization process according to claim 30, wherein said acid functional monomer is an ethylenically unsaturated carboxylic acid moiety containing monomer.

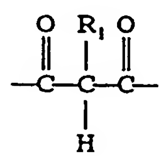
32. An addition polymerization process according to claim 31, wherein the polyfunctional amine is a non-polymeric functional amine having a chemical formula weight of less than about 2000 grams per mole.

33. An addition polymerization process according to claim 32, wherein said base is ammonia or a volatile amine.

34. An addition polymerization process according to claim 33, wherein the acetoacetoxy functional monomer is selected from the group consisting of acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, allyl acetoacetate, vinyl acetoacetate, 3-

(iii) a surfactant and (iv) an evaporable aqueous carrier, to an emulsion polymerization reaction zone;

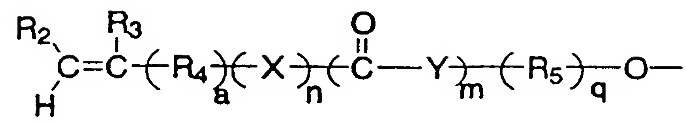
(b) introducing (i) first stage emulsion polymerizable ingredients to the emulsion polymerization reaction zone under emulsion polymerization conditions to form a first stage polymeric ingredient and (ii) subsequently introducing second stage emulsion polymerizable ingredients to the emulsion polymerization reaction zone under emulsion polymerization conditions to form a second stage polymeric ingredient, wherein at least one of the first stage and second stage emulsion polymerizable ingredients comprises independently (i) a monomer having pendant moieties having the ability to form stable enamine structures by reaction with amines which contain a divalent group of the structure



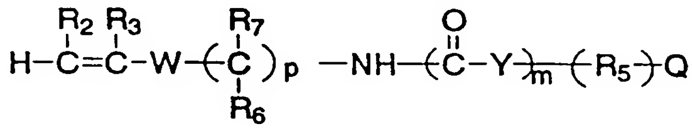
wherein R_1 is either H, a C_1 to C_{10} alkyl group, or phenyl, and (ii) an acid functional monomer;

(c) optionally introducing third stage emulsion polymerizable ingredients to the emulsion polymerization zone under emulsion polymerization conditions to form a third stage polymeric ingredient;

(d) adding an effective amount of base to the aqueous carrier to inhibit crosslinking of the second stage or third stage polymeric ingredient with a polyfunctional amine while both are present in the aqueous carrier; and



or



wherein R_2 is either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl, phenylalkyl, halo, CO_2CH_3 or CN;

wherein R_3 is either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl, phenylalkyl or halo;

wherein R_4 is either C_1 to C_{10} alkylene, phenylene, or substituted phenylene;

wherein R_5 is either alkylene or substituted alkylene;

wherein R_6 and R_7 are independently either H, C_1 to C_{10} alkyl, phenyl, substituted phenyl or phenylalkyl;

wherein any of a, m, n, p and q is either 0 or 1;

wherein each of X and Y is either —NH— or —O-;

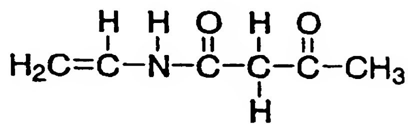
wherein W is arylene having 6 to 20 carbon atoms;

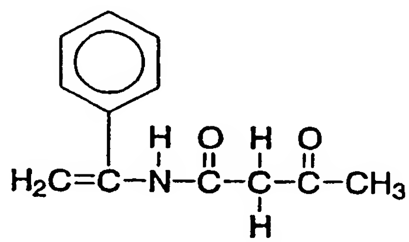
wherein Q is O or a single bond;

and wherein B is A, a C_1 to C_{10} alkyl group or phenyl, substituted phenyl, or heterocyclic.

polymeric ingredient is formed by the introduction of an ethylenically unsaturated monomer.

50. A multi-stage emulsion addition polymerization process according to claim 49, wherein said monomeric ingredient is selected from the group consisting of the structures of the formula.





and combinations thereof.

51. A multi-stage emulsion addition polymerization process according to claim 49, wherein the monomeric ingredient is selected from the group consisting of acetoacetoxyethyl methacrylate, acetoacetoxyethyl acrylate, allyl acetoacetate, vinyl acetoacetate, 3-isopropenyl-α,α-dimethylbenzyl amidoacetoacetate and combinations thereof.

52. A multi-stage emulsion addition polymerization process according to claim 51, wherein the non-polymeric polyfunctional amine is selected from the group consisting of 1,5-hexane diamine, hexamethylene diamine, 2-methyl pentamethylene diamine, 1,3-diamino pentane, dodecane diamine, 1,2-diamine, 3-methyl piperidine, isophorone diamine, bis-hexamethylene triamine, diethylene triamine, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/10877

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L51/00 C08L51/06 C08L33/14 C08K5/17 C09D151/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L C08F C08K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 764 699 A (ROHM & HAAS) 26 March 1997 see page 4, line 27 - page 6, line 11 see page 12, line 56 - line 58 see examples 1,9 ---	1-53
E	EP 0 854 153 A (ROHM & HAAS) 22 July 1998 see page 2, line 40 - page 3, line 42 see page 4, line 18 see example 3 ---	1-53
Y	WO 93 16133 A (JOHNSON & SON INC S C) 19 August 1993 cited in the application see the whole document & US 5 498 659 A ---	1-53

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
17 September 1998	28/09/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Andriollo, G

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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